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<p>A great variety of layered phosphonates and organophosphates of group(IV) metals, particularly zirconium, were prepared. The types of organic groups include polyethers, polyimines, pyridines, aryl and carboxyl. By using diphosphonates the organic groups can bridge across the layers to make rigid structures. If ethylphosphate or $H_2PO_4^-$ is mixed with the reactants, the bridging groups (or non-bridging groups) may be spaced along the layers. Manipulation of the synthetic method and choice of spacing then results in the production of a vast array of compounds with potential as catalysts, complexing and/or encapsulating agents, ion exchangers and ionic conductors.</p> <p>(continued on back)</p>									
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Title: Organic Derivatives of Group IV Phosphates

Objectives: To prepare a variety of organic derivatives of group(IV) metals in which the organic group is a phosphate or phosphonate. To explore the chemistry and potential uses of such compounds.

Background: Group(IV) cations, in particular Ti, Zr, Ge, Sn, Pb, form a variety of layered phosphates.¹ The two major classes, first prepared by Clearfield and his coworkers, are the α -type², $M(HPO_4)_2 \cdot H_2O$, and the γ -type³, $Zr(HPO_4)_2 \cdot 2H_2O$. The structure of α -Zr(HPO₄)₂·H₂O has been solved⁴ but not that of the γ -phase, which is reported to have a different layer type⁵. In 1978 Alberti, et al.⁶ reported the preparation of zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, which they indicated has the α -type structure (Fig. 1). Following this discovery, diphosphonate derivatives were prepared^{7,8} in which the organics crosslinked the layers. A notable example is $Zr(O_3PC_6H_4-C_6H_4PO_3)_2$ in which the distance between layers is 13.6Å compared to 7.6Å for the parent α -zirconium phosphate.

The crosslinked (often referred to as pillared derivatives because they prop open the layers) compounds have the pillars about 5.3Å apart. Since the van der Waals radii between benzene rings is 4Å, there is not much room between the pillars. In order to make these compounds useful as sorbants and catalysts, it is necessary to space the pillars farther apart. That was one of the objectives of this study.

Accomplishments:

A. Organically Pillared Derivatives

Two methods were used to space the biphenyl pillars; either phosphoric or phosphorous acid was added to the phosphonic acid or the pillars were spaced with ethylphosphate groups. Upon heating at 300°C, ethylene splits

out leaving behind a phosphate group. When the synthesis conditions are adjusted correctly, a single phase derivative such as pictured schematically in Fig. 2, is obtained. Pore size measurements as obtained from N_2 isotherms indicated a bimodal pore size distribution (Fig. 3A) with pores of mean radii of 9 and 20Å. The smaller pores correspond to the pillars spaced at every other position with inorganic phosphate and the larger pore spaced every third position i.e., 2 inorganic phosphates followed by a pillar. In contrast when the mixed derivatives are prepared by rapid precipitation a random pore size distribution, as shown in Fig. 3B, was obtained.

Sorption and catalysis studies with these derivatives was just getting underway when the project was terminated.

B. Mixed Derivatives of Layered Group(IV) Phosphates

By mixed derivatives, we mean those for which two different types of groups are present in the same solid particle. We have attempted to prepare these by reacting a mixture of either H_3PO_4 or H_3PO_3 or ethyl phosphate plus an organic phosphonate with a group IV cation. A resume of the results is given below.

1. Thermodynamically Controlled Synthesis - In the presence of a solubilizer such as HF, and long reflux times, two types of products are obtained: (1) either a mixture of two pure phases, one largely inorganic and the other largely organic, or (2) a staged product. The staged compounds have different layer structures depending upon the conditions of preparation. One of these is shown in Fig. 4. This compound is a particularly interesting one. It is recognized by its X-ray powder pattern for which $d_{001} = 22.3\text{\AA}$ i.e., the interlayer spacing is 22.3Å which is the sum of the two different layer spacings. By intercalating butylamine, a bilayer of amine is formed



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only in the -OH layer; and the combined interlayer spacing sensed by X-rays is now 33.3Å. When butylamine is intercalated into zirconium phosphate, the interlayer spacing expands from 7.6Å to 18.8Å. Thus, in the staged compound the new repeat distance is $18.8 + 14.7 = 33.3\text{\AA}$. Calcium ion was also exchanged into the -OH layer producing the sequence $-\text{O}_3\text{ZrO}_3\text{P}-\text{OCaOPO}_3\text{ZrO}_3\text{P}-\phi$, etc.

2. Kinetically Controlled Experiments - By omitting the HF and refluxing for short periods of time, mixed derivatives of the type shown in Fig. 5 are formed. The 12.5Å derivative was obtained on refluxing for one hour while the 10.3Å phase formed on refluxing overnight. Sulfonation of these derivatives was carried out to provide compounds with unusual properties (see below).

C. Functionalized Derivatives

1. Sulphonated Derivatives. - Both the pillared and unpillared aryl derivatives may be sulphonated by treatment with fuming sulfuric acid. Such products are depicted schematically in Fig. 6. The unpillared derivative swells in water and if sufficient sulfonic acid groups are present may go into colloidal suspension. The complexing behavior of these compounds is shown in Table 1. Note that the larger the species to be complexed, the greater is the affinity for the unpillared derivative (row 1, Table 1). Thus, encapsulation of large cationic species is almost quantitative (see use in photochemistry in section D below). In contrast the crosslinked derivatives cannot swell and are able to exclude large species.

2. Amine Derivatives. - Benzyl and ethyl pyridine derivatives were prepared. These are depicted in Figs. 7 and 8, respectively, and should be compared to

the phenyl derivative shown in Fig. 1. These figures illustrate the positioning of the rings in the interlayer space as determined from computer models, using potential calculations and the structure of the α -zirconium phosphate layer as a base.

An interesting feature of the amine derivatives is their ability to complex transition metals. Upon addition of acid to the amine derivatives they swell, increasing the interlayer distance. In acid solution the swollen resins behave as anion exchangers. However, if a transition metal is added to the swollen protonic phase and base added, the amount of transition metal incorporated is a function of the pH, i.e., the higher the pH the greater the complexing. Exploitation of these phenomena was in progress at the termination of the grant and will be discussed below on the section on polyimines.

D. Photochemistry

We have shown in Table 1 that the sulfonated, uncrosslinked arylphosphonate phosphate, $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})(\text{HPO}_4)$, encapsulates large complexes. This compound was made to incorporate a mixture of $\text{Ru}(\text{bipy})_3^{2+}$ and methyl viologen into the layers. Exposure to sunlight produced a rapid transformation of Ru^{2+} to Ru^{3+} by electron transfer to the amine. The ruthenium bipyridyl cation was used to probe the chemical environment within the sulfonate layers⁹. The $\text{Ru}(\text{bipy})_3^{2+}$ intercalate exhibited pronounced spectral shifts in both its absorption and emission spectra, relative to its aqueous solutions. The observed shifts were found to result from interactions of the ruthenium complex with the phenyl rings of the host layers. This phenomenon is thus different than changes ascribed to the ruthenium bipyridyl when incorporated into clays, micelles or vesicles. The

next step will be to obtain data on the rates of electron transfer.

By sulfonating the staged compound shown in Fig. 4, we obtained a staged compound in which alternate layers contained aryl sulfonic acid groups and HPO_4^{2-} groups. We were attempting to place $\text{Ru}(\text{bipy})_3^{2+}$ all in the sulfonate layer and methylviologen in the phosphate layers in the expectation that electron transfer would now occur as a burst. Although these reactions are important as potential water splitting techniques, the work has been suspended pending our obtaining additional funding.

E. Polyether and Polyimine Derivatives

Polyether mono- and diphosphonates of polyethylene oxide, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{-H}$, with $n = 1, 2, 4, 9, 13, 22$ were prepared. Both crosslinked and uncrosslinked layered derivatives of $\text{Zr}(\text{IV})$ and $\text{Ti}(\text{IV})$ were synthesized. A schematic representation of the uncrosslinked derivative for which $n = 4$ is shown in Fig. 9. These compounds were able to complex electrolytes such as NaCNS , CuCl_2 and PdCl_2 whereupon they became ionic conductors. As n increases, the swelling power in water also increases to the point where derivatives with $n > 9$ colloiddally disperse in water. In addition the solid becomes more gel-like. In general, the polyethers were found to be relatively weak complexing agents. This behavior may stem from the fact that the polyether chains coil in such a way as to direct the oxygen unpaired electrons in towards the center of the coil¹⁰. It was felt that this would not be the case if the oxygens were replaced by nitrogen.

Following the above lead polyimine derivatives in which the repeat unit is $\text{H}_2\text{N}(-\text{CH}_2\text{CH}_2\text{NH}-)_n$ with $n = 1, 2, 3, 4$ were prepared. Several variations on this theme were accomplished. For example, with $n = 1, 2$ polyimine phosphates as well as phosphonates were prepared. In addition for both

phosphates and phosphonates, bridged derivatives were synthesized. Finally, when the imines were prepared by a Mannich type reaction the phosphonate was of the type $\text{H}_2\text{O}_3\text{P}-\text{CH}_2(\text{NHCH}_2\text{CH}_2)_n-\text{NH}_2$. A small sampling of the compounds prepared (in all 38 different compounds were synthesized) is listed in Table II. All of these compounds were found to be powerful complexing agents as witnessed in the representative titration curves (Figs. 10, 11) in the presence of Cu^{2+} . The exact way in which the metal ions are complexed are not known but UV-visible spectra coupled with other spectroscopies and computer modelling of possible complexes which reproduce the titration curves will be utilized to solve this problem.

As an aside it should be noted that the bridged compounds are most intriguing. If the lone pairs point toward each other, both in the bridged polyethers and imines, then we might expect to see crown ether or porphorin type complexing. This phase of the work will be continued as soon as new funding is identified.

F. Organic Derivatives of Group II and Group III elements.

It was discovered¹¹ that both group II and group III elements (Al^{3+} , Fe^{3+} , Cr^{3+}) form phosphonates and to a lesser extent organic phosphates. Representative phosphonates of Mg^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} were prepared. They have the general formula $\text{M}(\text{O}_3\text{PR})\cdot\text{H}_2\text{O}$ (R = aryl or alkyl group) and have layered structures (Fig. 12) in which the layers are similar to those in $\text{NH}_4\text{Zn}(\text{PO}_4)\cdot\text{H}_2\text{O}$.¹² However, it was also found that linear chain type compounds as well as layered compounds can also be prepared. An example of a new layer type is illustrated in Fig. 13 and shows the structure of $\text{Zn}(\text{O}_3\text{POC}_2\text{H}_5)\cdot\text{H}_2\text{O}$ projected down the c axis, while in Fig. 14 is shown the single chain structure of $\text{Zn}(\text{O}_3\text{PCH}_2\text{NH}_2^+\text{CH}_2\text{CH}_2\text{NH}_3^+)\text{Cl}_2$. It should be noted

that both nitrogens of the amino-ligand in this compound are protonated and, as illustrated in Fig. 15, they cause the chain to twist so that the amino-group forms hydrogen bonds with Cl^- and oxygens of the phosphonate group.

With trivalent cations a totally different series of compounds is formed in which the composition is dependent upon the pH. Below a pH of 2 the compounds have a general formula represented by $\text{M}(\text{O}_3\text{PR})_y(\text{HO}_3\text{PR})_x \cdot n\text{H}_2\text{O}$ where $2y+x = 3$. Above this pH some of the organic groups are replaced by hydroxyls with the amount of OH increasing as the pH at which the solid is precipitated is increased. The structures of these compounds have not been determined (poor crystals) but based on their X-ray powder patterns they appear to be layered.

G. Zinc Phosphites

The results of the previous section led us to consider mixing in H_3PO_3 with the organic phosphonates to space the organic ligands in the group (II) and group (III) derivatives. However, as a preliminary experiment we first prepared a zinc phosphite, which crystallized from solution as $\text{Zn}(\text{HO}_3\text{PH})_2 \cdot 4\text{H}_2\text{O}$. To our surprise, the crystals had a very large unit cell in the hexagonal system of $a = 21.128(2)$ $c = 7.769(6)\text{\AA}$ and gave a cavity type structure as shown in Fig. 16. The cavity is about 7\AA in diameter which puts it in the medium size zeolite class. On titration with NaOH in methyl alcohol, the compound reacted to yield a totally new structure as shown in Fig. 17 in which all the sodium was sequestered from solution. If this reaction is reversible, we will have obtained an extremely interesting new sequestering agent. The selectivity of the compound as a function of ion size and charge is under investigation as well as the type of phosphites formed by other cations.

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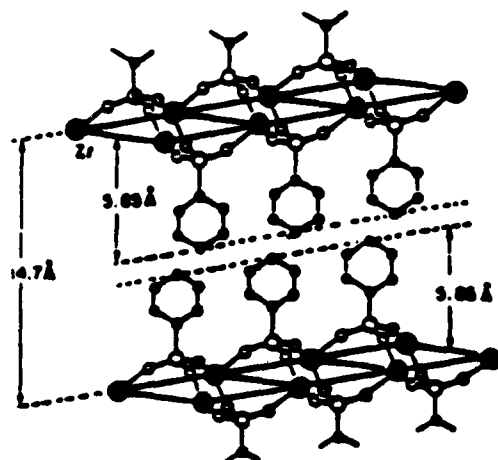


Fig. 1. Idealized crystal structure of zirconium bisphosphonate. Zr: O, P: a, b, c.

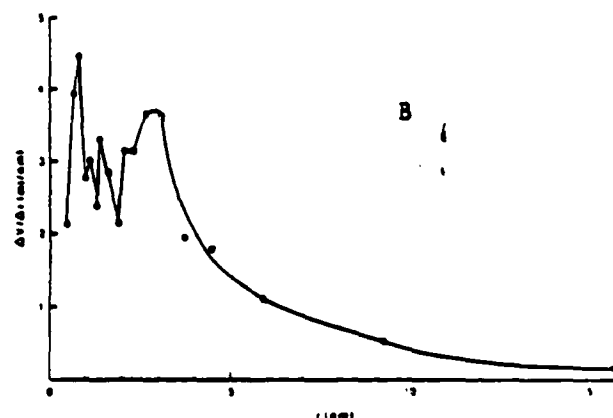
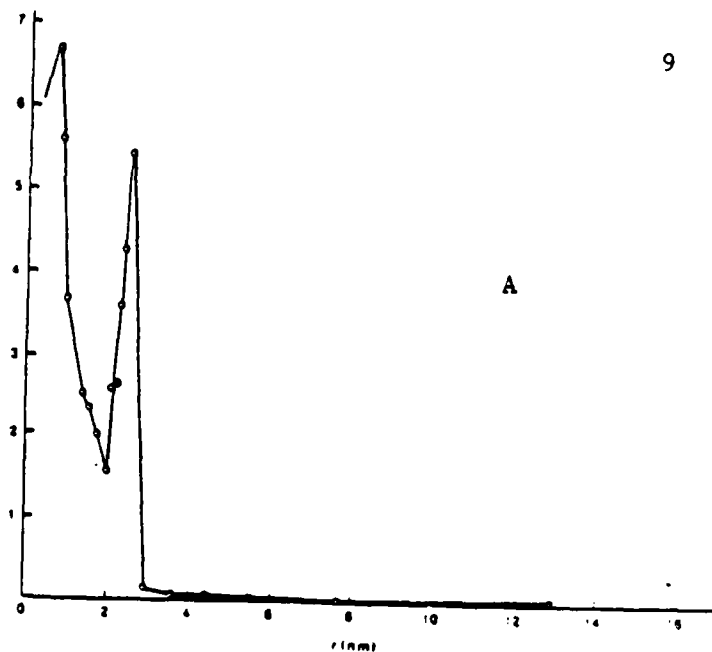


Fig. 3. Pore size distribution curves of pillared zirconium phosphates: (A) - Bimodal pore size distribution ($r \approx 9$ and 21 \AA) obtained from compound illustrated in Fig. 1 prepared by homogeneous precipitation. (B) - Random pore size distribution obtained by rapid precipitation.

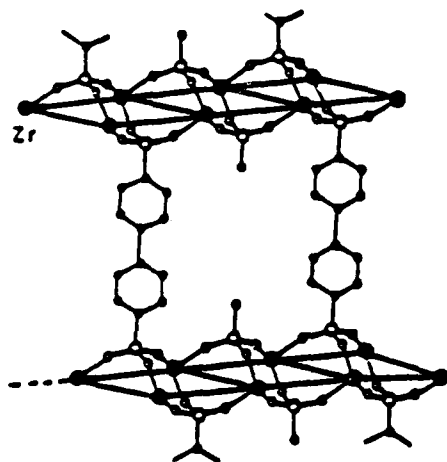


Fig. 2. Schematic representation of biphenyl pillared (cross-linked) layers of zirconium phosphate. The ideal composition is $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_4-\text{C}_6\text{H}_4\text{PO}_3)_{0.5}(\text{HPO}_4)$.

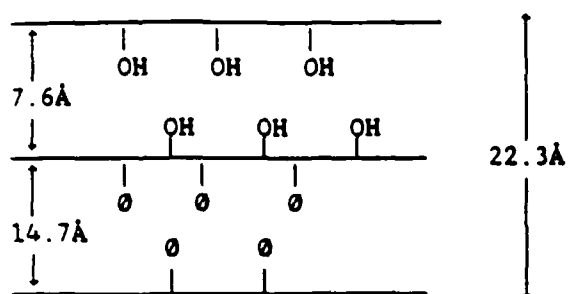
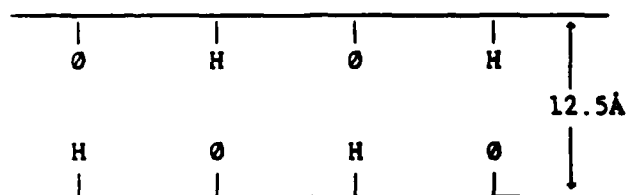
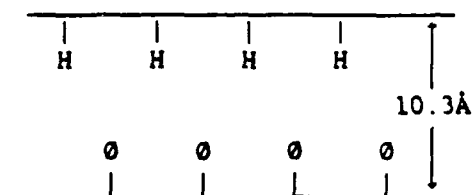


Fig. 4. Schematic drawing of staged zirconium phosphate phenyl phosphonate showing how the layer 22.3Å lattice spacing represents a $P-O_3-Zr-O_3P$ layer.



A



B

o = phenyl group

Fig. 5. Kinetic or non-equilibrium preparations lead to mixed derivatives such as (A) obtained by refluxing for a short time and (B) obtained by refluxing for a long time the rapidly precipitated zirconium phosphite phenyl phosphonate.

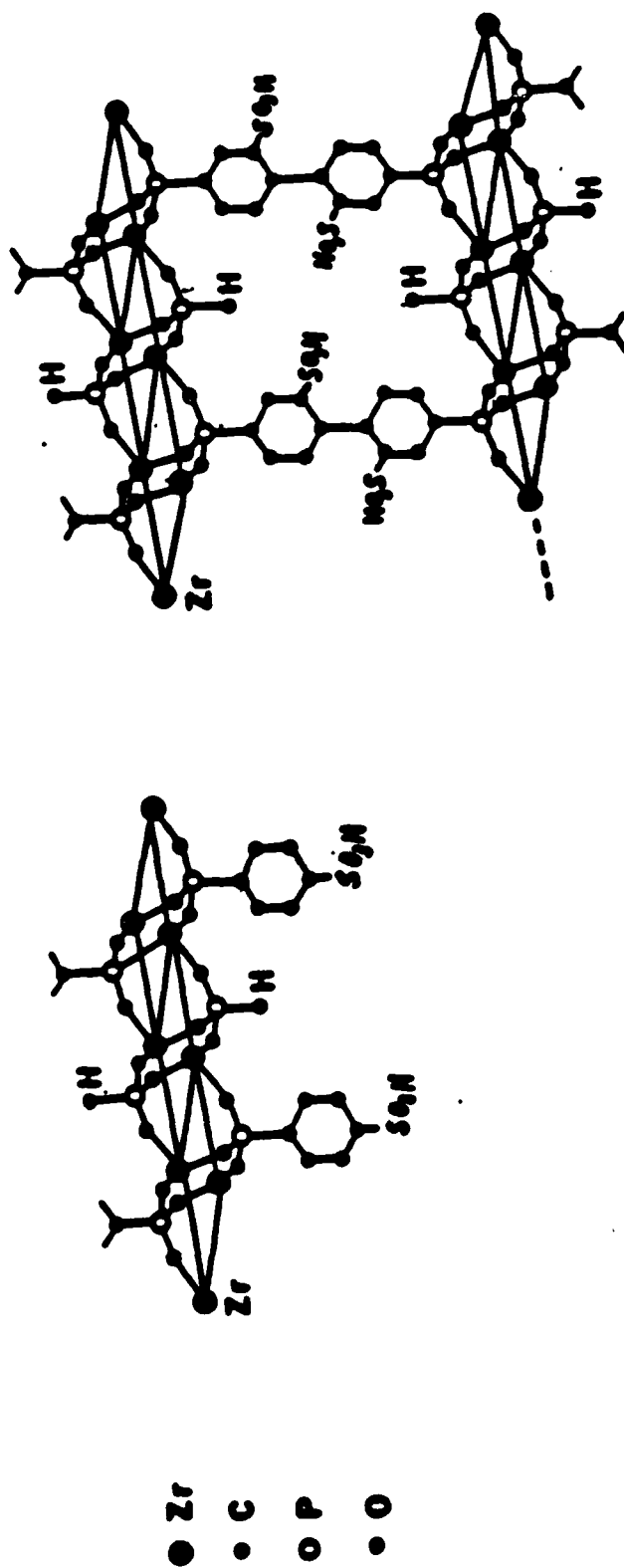


FIGURE 6. IDEALIZED CRYSTAL STRUCTURE OF LAYERED ZIRCONIUM PHOSPHONATES CONTAINING PENDANT SULFONIC ACID GROUPS.

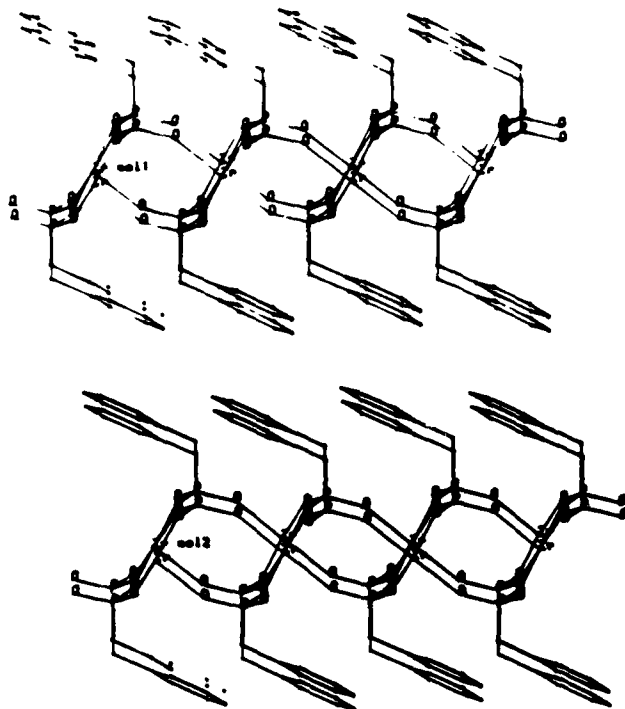
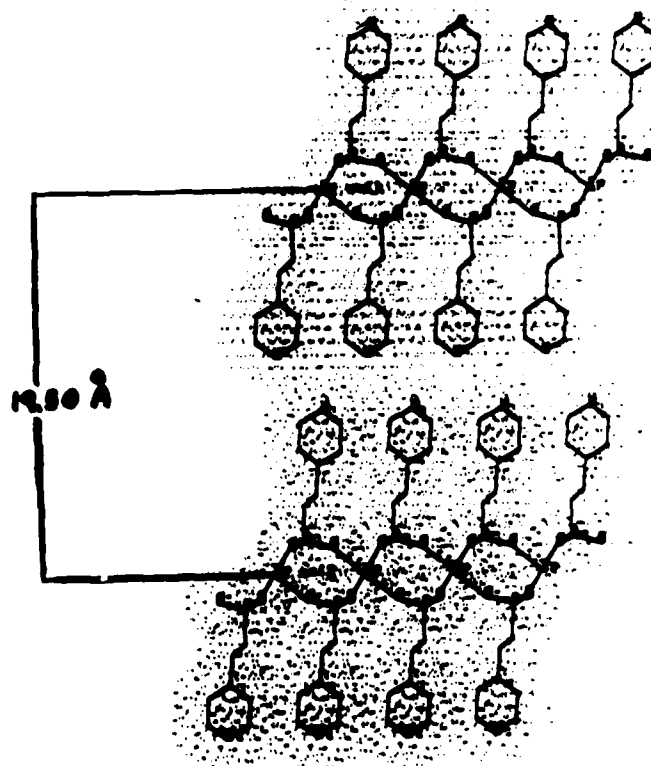


Fig. 7. Computer simulated model of $\text{Zr}(\text{O}_3\text{PCH}_2\text{C}_6\text{H}_5)_2$ looking down the b-axis. The phenyl rings are $\sim 5\text{\AA}$ apart in the b-direction.

Fig. 8. Computer simulated model of $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{-C}_6\text{H}_4\text{-N})_2$. The dotted areas indicate the extent of van der Waals forces and predict an interlayer spacing of 19.5\AA . Measured value is 19.



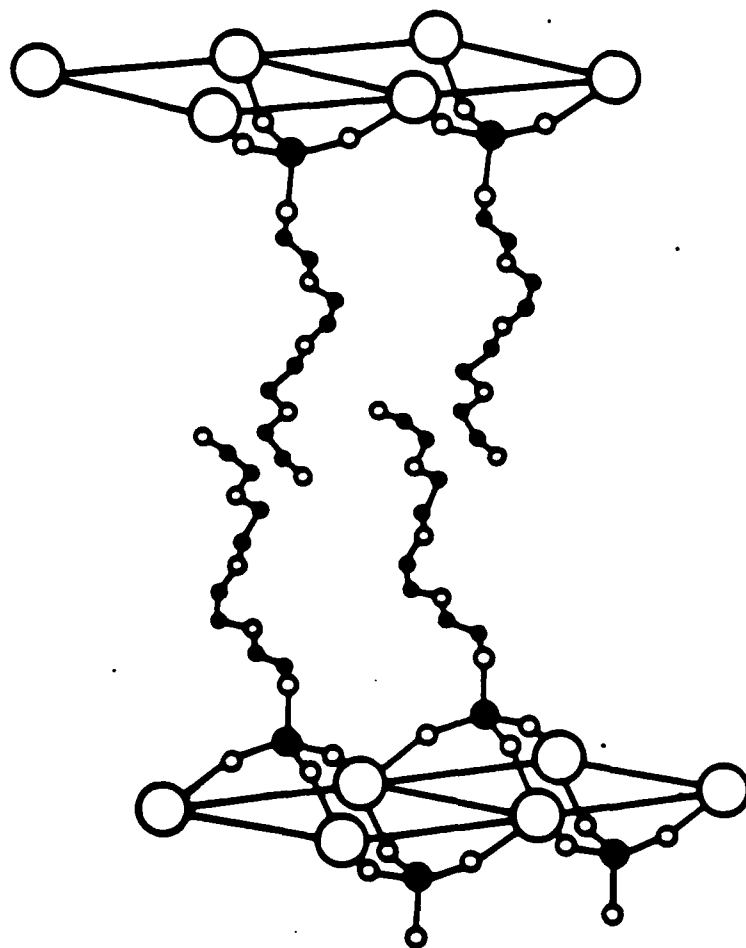
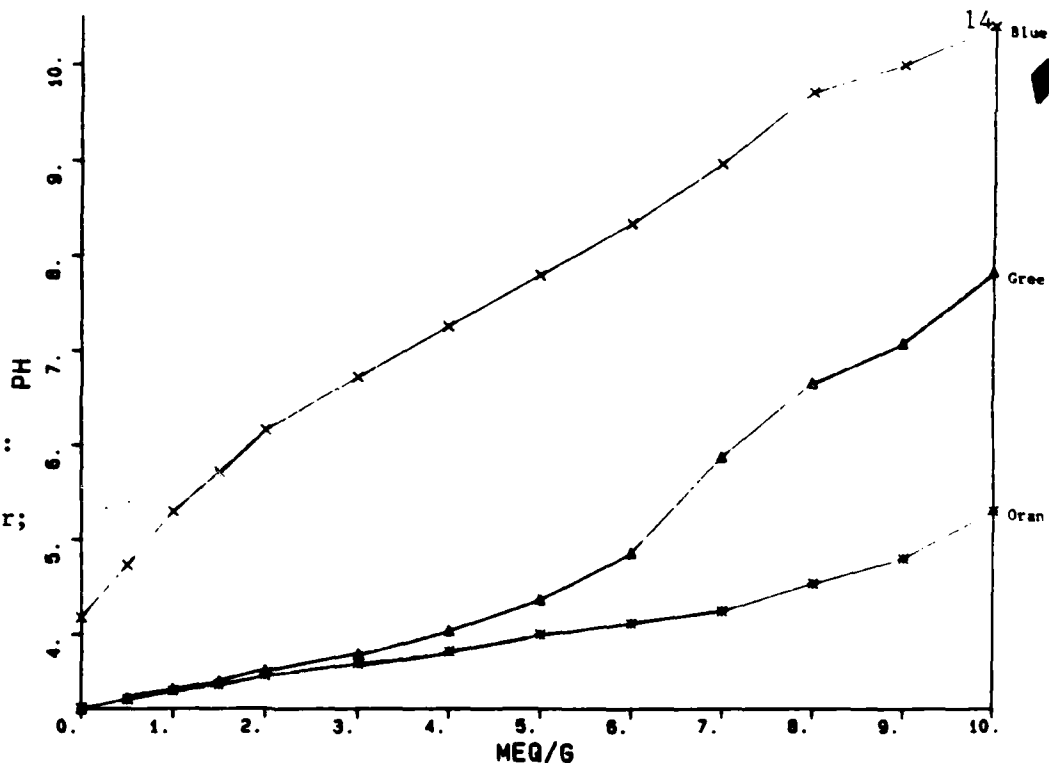


Fig. 9. Schematic representation of tetraethylene glycol ester of α -zirconium phosphate. O,Zr; \bullet ,P; \circ ,O; \bullet ,C.

Fig. 10.

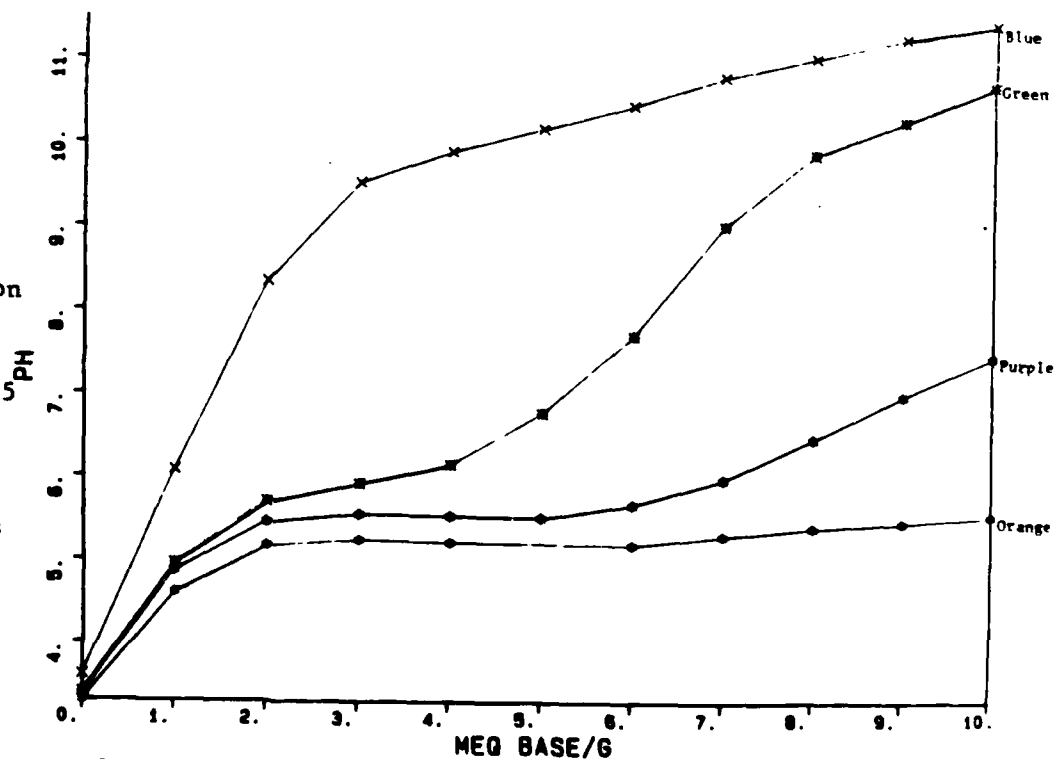
Potentiometric titration curves for $\text{Zr}(\text{O}_3\text{PCH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)_2$:
 X, no added Cu^{2+} ; Δ , 1 mole added Cu^{2+} /mg Zr ;
 *, 2 moles added Cu^{2+} /mole Zr . Titrant is 0.1M NaOH.



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Fig. 11.
 Potentiometric titration curves for the cross-linked layered $\text{Zr}(\text{O}_3\text{PCH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{PO}_3)_{0.5}(\text{HPO}_4)$. X, no added Cu^{2+} ;
 * 0.5 moles added Cu^{2+} /mole Zr ; Δ , 1 mole added Cu^{2+} /Zr (purple); + (orange) 2 moles added Cu^{2+} /Zr



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Note the pancake shape of the thermal ellipsoids of the phenyl group indicative of rotation about the P-C bond.

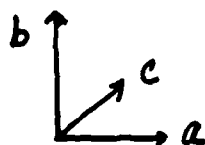
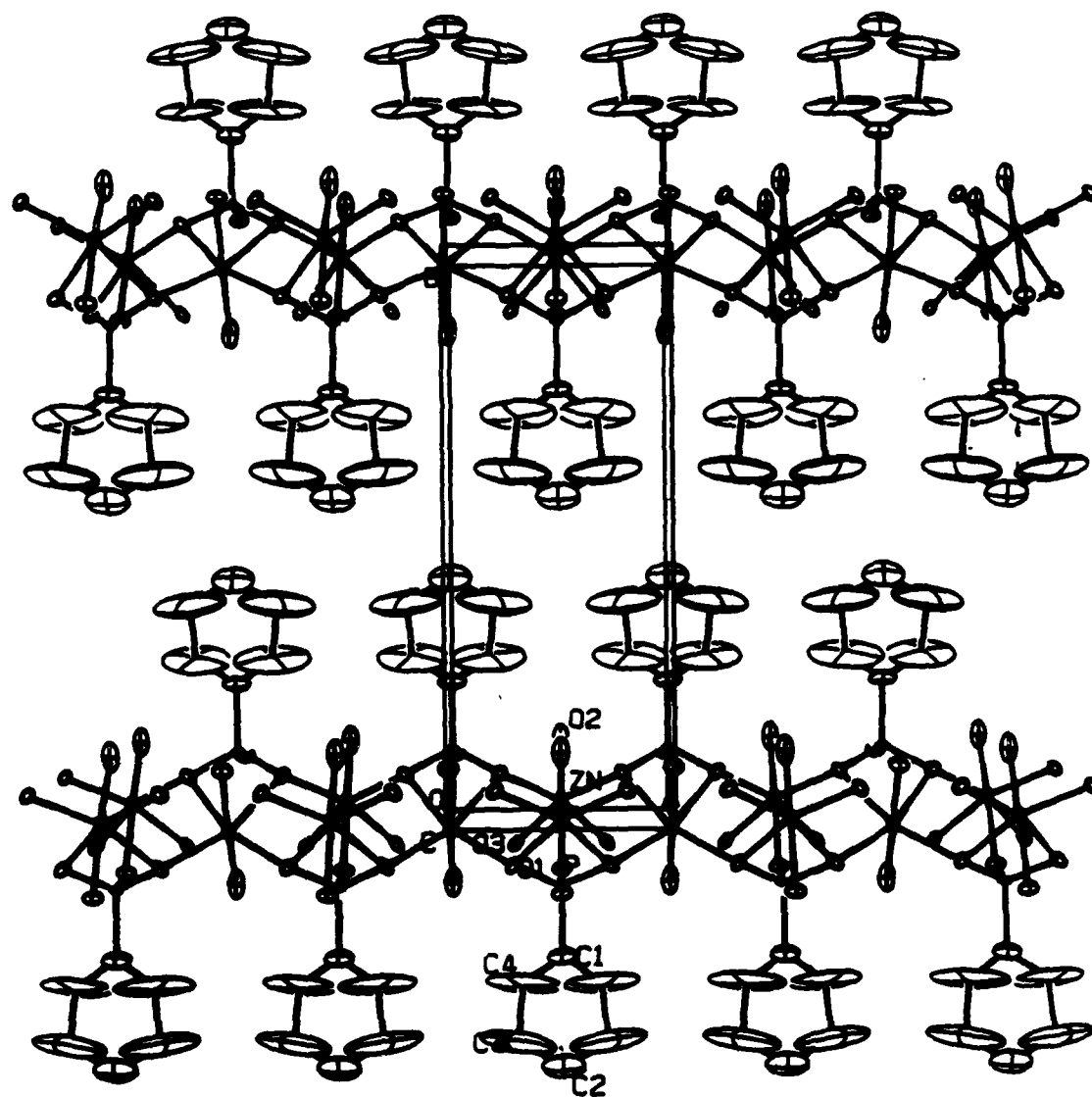


Fig. 12

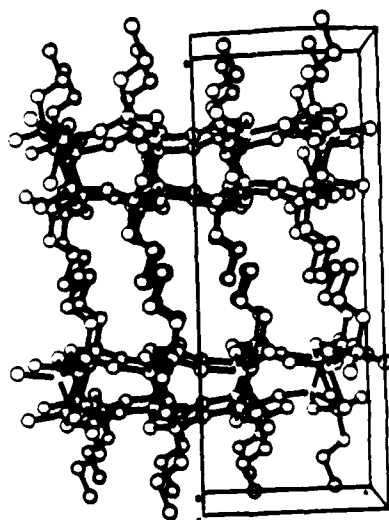


Fig. 13

Zn(O₃POC₂H₅)·H₂O

Crystal structure of $\text{Zn}(\text{O}_3\text{POC}_2\text{H}_5) \cdot \text{H}_2\text{O}$ projected down the C-axis. The solid lines outline a unit cell. In 3-dimensions the layers undulate up and down along C so that in projection it appears as though a double chain of atoms runs parallel to the a-direction.

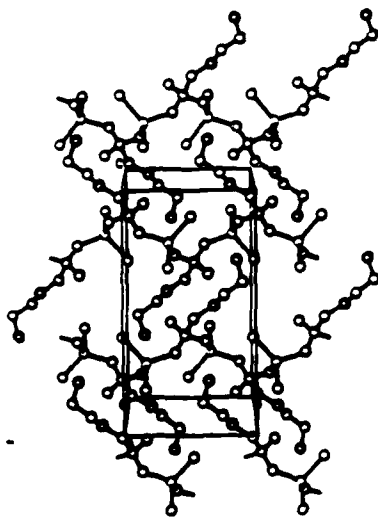


Fig. 14

Zn(O₃P-CH₂NH₂CH₂CH₂NH₃⁺)Cl₂

Schematic view of the crystal structure of $\text{Zn}(\text{O}_3\text{P-CH}_2\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+)\text{Cl}_2$. The zinc atoms are bridged by phosphonate oxygens forming chains parallel to a.

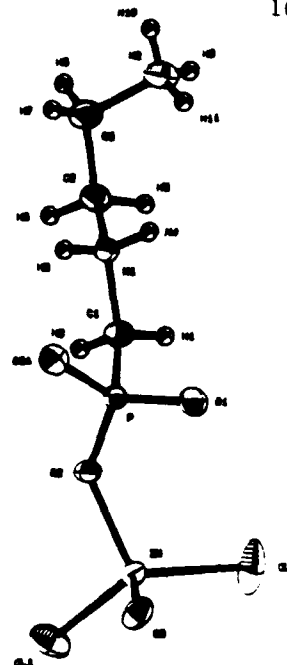


Fig. 15

Expanded view of coordination around the zinc atoms showing the conformation of the amino-phosphonate (from compound in Fig. 14).

Fig. 16.
 Crystal structure of zinc
 monohydrogen phosphite,
 $\text{Zn}(\text{HPO}_3\text{H})_2 \cdot 4\text{H}_2\text{O}$. There are
 six zinc phosphite units forming
 the large cavities in which the
 water molecules (not shown)
 reside.

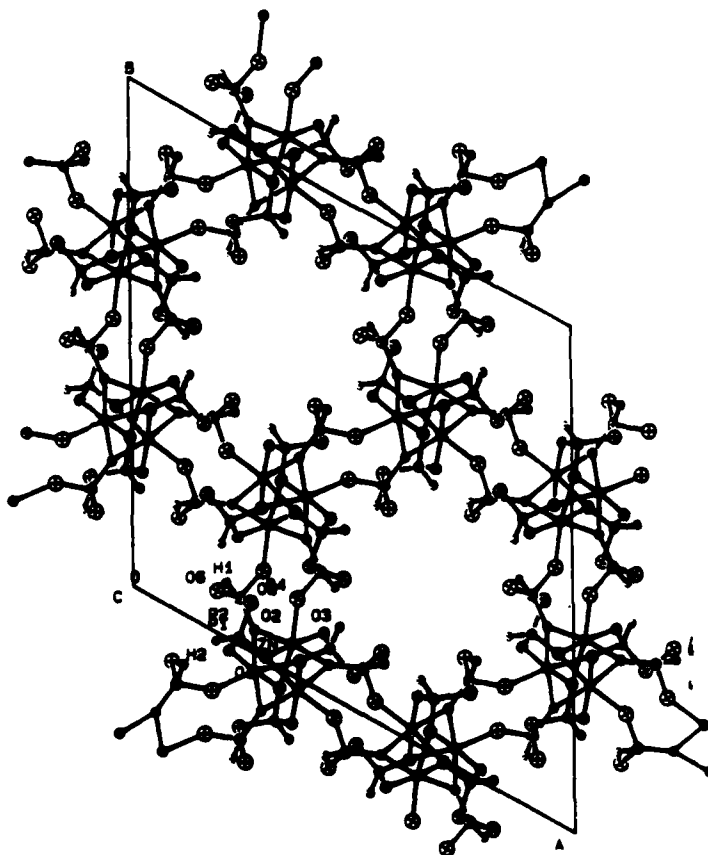


Fig. 17.
 The crystal structure of a
 sodium zinc phosphite formed
 by addition of NaOH to the
 compound shown in Fig. 14.

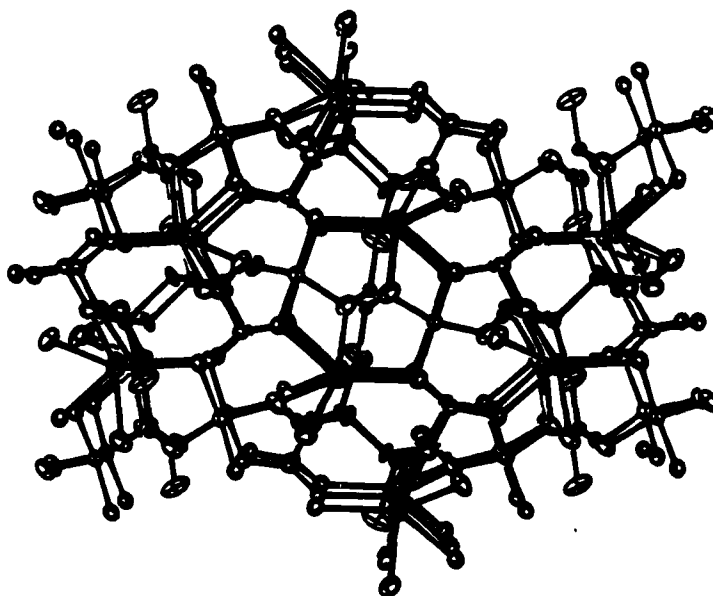


TABLE 1

TYPICAL K_D VALUES (M_L/θ)
CONC (10^{-3} M)

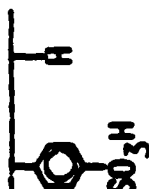
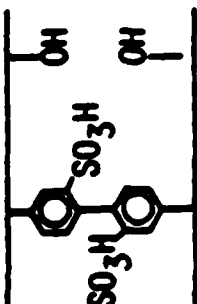
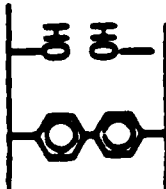
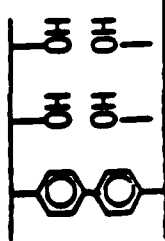
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MY-IV-16-SO ₃ H	52	108	335	-	249	20400	33250	30100
								
MY-IV-70-SO ₃ H	78.5	58.7	157	149	107	1110	<1	<1
								
MY-IV-70	18.2	7.75	25.7	262	195	894	58.0	-
								
MY-IV-84	-	-	-	312	291	963	<1	<5

Table 2. Interlayer Spacings of the zirconium polyimine Derivatives of the Type $\text{Zr}(\text{RPO}_3)_x (\text{R}'\text{PO}_3)_{2-x}$

Compound No.	R	R'	X	Interlayer Spacing (Å)
V-26	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2-$	-	2	17.1
V-36	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2-$	-OH	0.63	14.5
IV-96	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2-$	-H	1.35	Amorphous
V-24	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2-$	-	0.9	
IV-72	$\text{O}_3\text{P}-\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2-$	-	1 ^a	13.8
IV-96	$\text{O}_3\text{P}-\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2-$	-OH	0.38	9.5
IV-97	$\text{O}_3\text{P}-\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2-$	H	0.94	Amorphous
V-38	$\text{O}_3\text{P}-\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2-$	-OH	0.5	

^aThe cross linked derivatives have the general formula

